

Charge and Orbital Ordering and Spin State Transition Driven by Structural Distortion in YBaCo₂O₅

S. K. Kwon and B. I. Min

Department of Physics, Pohang University of Science and Technology, Pohang 790-784, Korea
(February 1, 2008)

We have investigated electronic structures of antiferromagnetic YBaCo₂O₅ using the local spin-density approximation (LSDA) + U method. The charge and orbital ordered insulating ground state is correctly obtained with the strong on-site Coulomb interaction. Co²⁺ and Co³⁺ ions are found to be in the high spin (HS) and intermediate spin (IS) state, respectively. It is considered that the tetragonal to orthorhombic structural transition is responsible for the ordering phenomena and the spin states of Co ions. The large contribution of the orbital moment to the total magnetic moment indicates that the spin-orbit coupling is also important in YBaCo₂O₅.

PACS number: 75.50.Ee, 71.27.+a, 71.20.Be, 71.70.Ej

Recently, an interesting spin state transition of the Co²⁺ ion in YBaCo₂O₅ has been reported by Vogt *et al.* [1] using the neutron powder diffraction (NPD) measurements. The transition is induced by the long-range orbital and charge ordering of Co²⁺/Co³⁺ ions. The ordered oxygen-deficient double perovskite RBaCo₂O_{5+ δ} (R = rare-earths) [2] has attracted much attention as a new spin-charge-orbital coupled system like manganites and also as a new Co-based colossal magnetoresistance (CMR) material. Indeed, giant magnetoresistance are observed for R =Gd and Eu, $(\rho_0 - \rho_{H=7T})/\rho_0 = 41\%$ and 40% for GdBaCo₂O_{5.4} and EuBaCo₂O_{5.4}, respectively [3].

In the paramagnetic phase, YBaCo₂O₅ is crystallized in the tetragonal structure of the space group $P4/mmm$. It consists of double CoO₅ square base pyramidal backbone layers along the c -axis in which Y and Ba layers intervene alternatively and oxygens are deficient exclusively from the Y layers [2–4]. According to the valency consideration, Co²⁺ and Co³⁺ ions coexist similarly as the Mn³⁺/Mn⁴⁺ covalency in hole-doped La_{1- x} Sr _{x} MnO₃. Below $T_N \sim 330$ K, YBaCo₂O₅ undergoes a G -type antiferromagnetic (AFM) transition and the lattice changes slightly from the tetragonal to orthorhombic structure [1]. At $T_{CO} \sim 220$ K, a pronounced upturn is observed in the resistivity indicating that another transition takes place, *i.e.*, the long-range charge and orbital ordering of Co²⁺/Co³⁺ ions. The stripe type charge ordering is formed in the ab plane. Further, the spin state of the Co²⁺ ion changes from the low to high spin across T_{CO} , which is evidenced by the increased magnetic moment per Co ion from $2.10\mu_B$ at 300 K to $3.45\mu_B$ at 25 K. More recently, for the isostructural HoBaCo₂O₅, essentially the same features are observed of $T_N \sim 340$ K and $T_{CO} \sim 210$ K [5].

The phenomenon of the spin state transition is observed usually in cobaltates such as LaCoO₃ and La_{1- x} Sr _{x} CoO₃. In LaCoO₃, the magnetic ground state of Co³⁺ ion corresponds to the low spin (LS) state with $t_{2g}^6 e_g^0$. Upon heating, a successive spin state transition to an intermediate spin (IS) state and then to a high spin (HS) state occurs [6]. Note that, distinctly from the case

in LaCoO₃, the spin state transition in YBaCo₂O₅ seems to occur for Co²⁺ ion. In fact, this issue is still controversial. Based on the reduction of the magnetic susceptibility below 220K, Akahoshi and Ueda [7] suggested that the AFM transition takes place at $T \sim 220$ K which is associated with a spin state transition of Co³⁺ from the HS to LS state upon cooling. Thus, the nature of the spin state transition and the interplay of the spin state with the charge and orbital ordering are still unclear.

To reveal the mechanism of the spin state transition as well as the charge and orbital ordering, we have explored the electronic structure of the G -type AFM YBaCo₂O₅ using the local-spin density approximation (LSDA) + U scheme implemented in the linearized muffin-tin orbital band method [8,9].

We have employed two structural data of nearly tetragonal structure at 300 K (L1) and orthorhombic structure at 25 K (L2) [1]. In the L1 structure, all the Co sites have an equal average bond length of $d(\text{Co-O}) = 1.97$ Å. Whereas in the L2 structure, there are two different kinds of Co sites, CoI and CoII. The bond length at CoI sites is extended to $d(\text{CoI-O}) = 2.03$ Å and that at CoII sites becomes shortened to $d(\text{CoII-O}) = 1.92$ Å. The G -type AFM spin order is assumed in all our calculations.

In Fig. 1, we have compared the LSDA Co $3d$ partial density of states (PDOS) for the L1 and L2 structures. Most notable is the change of the exchange splitting which becomes larger for CoI site and smaller for CoII in L2 than that for Co in L1. This indicates that, due to the lattice distortion, $3d$ electrons in L2 becomes more localized for CoI and less localized for CoII in comparison to those for Co in L1. The calculated spin magnetic moments are $\mu_S = 1.68\mu_B$ and $0.95\mu_B$ for each CoI and CoII site, respectively, in L2 and $\mu_S = 1.13\mu_B$ for Co in L1. The sizes of the spin moments are consistent with the degree of $3d$ electron localization. Hence, the LSDA gives a qualitatively good information about the structural transition effects on Co $3d$ electron states. The LSDA, however, yields an incorrect metallic ground state which pertains even after the structural transition from the L1 to L2 structure. This is different from the experiment which shows unambiguously the semiconducting

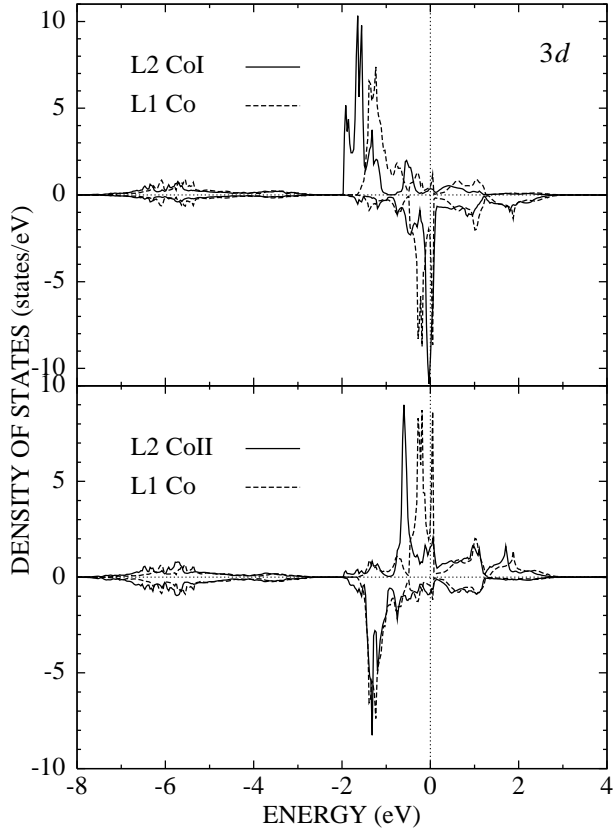


FIG. 1. The LSDA PDOS of Co 3d electrons in the L1 (300 K phase) and L2 (25 K phase) structures. In L2, there are two different types of Co sites, CoI and CoII. Neighboring CoI and CoII sites are polarized antiferromagnetically. As manifested by the exchange splitting, 3d electrons are more localized for CoI site and less localized for CoII than those for Co in L1.

resistivity behavior below 220 K [1,5,7].

Using the LSDA, one cannot expect proper description of localized Co 3d electrons in YBaCo_2O_5 . To resolve the above problem, we have applied the LSDA + U method with parameter values of $U = 5.0$ eV and $J = 0.89$ eV. Although there is an arbitrariness of the U -value in our calculation, the LSDA + U results are usually not much sensitive to the used U -value within $\Delta U \sim \pm 1$ eV [10]. The spin-orbit interaction is also taken into account in the self-consistent variational loop, because Co 3d electrons are expected to retain atomic properties to some extent due to their localized nature.

Figures 2 and 3 present CoI and CoII 3d PDOS, respectively, in the L2 structure obtained by the LSDA + U calculations. In the bottom panels, t_{2g} and e_g decompositions of 3d PDOS are also provided. It is amusing to note that the energy gap of $E_g \sim 0.6$ eV opens at the Fermi level E_F and so YBaCo_2O_5 becomes an insulator as expected in consideration of the $\text{Co}^{2+}/\text{Co}^{3+}$ charge ordering. For CoI 3d electrons, the majority-spin bands are fully occupied by three electrons in t_{2g} and two electrons in e_g bands. The minority-spin t_{2g} bands are only

partially occupied by two electrons, and one t_{2g} and two e_g bands are almost empty. Considering the pyramidal environment of Co, the occupied t_{2g} states corresponds to d_{zx} and d_{yz} while the empty t_{2g} to d_{xy} . Accordingly, the nominal valency and the 3d electron configuration at CoI site are assigned to be Co^{2+} and $3d^7$ ($t_{2g}^5 e_g^2$), respectively [11]. Hence, Co^{2+} ion is in the HS state with spin magnetic moment of $\mu_S = 3\mu_B$ ($S = 3/2$), which is consistent with the NPD data.

For CoII 3d electrons, the majority-spin bands are not fully occupied with a split-off empty e_g state above E_F (see Fig. 3). For the minority-spin bands, the situation is similar to the case of CoI. It is thus possible to identify the 3d electron configuration of CoII as $3d^6$ ($t_{2g}^5 e_g^1$) and the valency as Co^{3+} . With one less electron than Co^{2+} , the lower $d_{3z^2-r^2}$ out of two e_g states in the majority-spin bands is occupied and the upper $d_{x^2-y^2}$ becomes empty. Hence, the spin state of Co^{3+} ion is the IS state which is also in agreement with the experimental analysis of $\mu_S = 2\mu_B$ ($S = 1$).

The calculated charge occupancies of each Co 3d orbitals are shown in Table I. For Co^{2+} ion, the majority-spin bands are almost completely occupied by $t_{2g} \uparrow = 2.98$ and $e_g \uparrow = 1.99$ electrons, while the minority-bands are only partially occupied by $t_{2g} \downarrow = 2.02$ and $e_g \downarrow = 0.37$ electrons. For Co^{3+} ion, it is noticeable that the majority-spin e_g states are partially occupied by $e_g \downarrow = 1.54$ electrons. Hence, the calculated charge occupancies are consistent with the nominal valencies of Co^{2+} and Co^{3+} , if one takes into account the band hybridization effects.

Vogt *et al.* [1] have deduced magnetic moments from the NPD experiments as $\mu_{\text{exp}} = 4.2\mu_B$ and $2.7\mu_B$ for each Co^{2+} and Co^{3+} ion, respectively. In the analysis of the experiments, they counted only the spin moment contribution, assuming that the orbital moment is quenched. However, the orbital moment is only partially quenched in YBaCo_2O_5 . In Table I, we have summarized the calculated magnetic moments using the LSDA + U

TABLE I. The calculated charge occupancies of Co 3d orbitals (electrons) and magnetic moments (μ_B) of YBaCo_2O_5 in the LSDA + U method.

	Co^{2+}	Co^{3+}
$t_{2g} \uparrow$	2.98	2.14
$e_g \uparrow$	1.99	0.60
$t_{2g} \downarrow$	2.02	2.99
$e_g \downarrow$	0.37	1.54
μ_S	2.61	1.84
μ_L	1.04	0.40
μ_{tot}	3.65	2.24
μ_{exp}	$4.2^a, 3.7^b$	$2.7^{a,b}$

^a Reference [1].

^b $\text{HoBaCo}_2\text{O}_5$ in Ref. [5]. The assignment of the magnetic moments to each Co ion is corrected (see text).

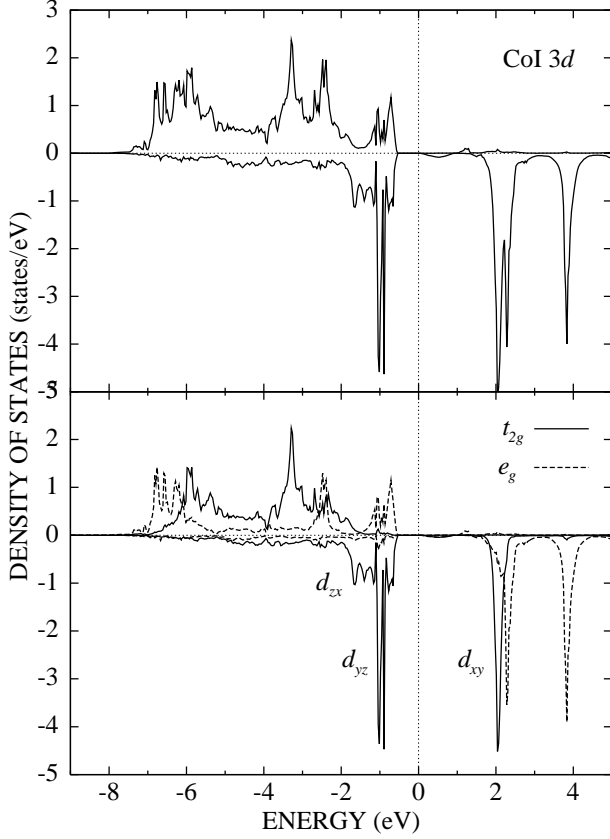


FIG. 2. The LSDA + U PDOS of CoI 3d electrons in the L2 (25 K phase) structure. In the bottom panel, t_{2g} and e_g decompositions of 3d PDOS are also provided. The majority-spin bands are fully occupied, while in the minority-spin bands, only 2/3 states of t_{2g} bands are occupied. The nominal valency of CoI site is Co^{2+} with $3d^7$ ($t_{2g}^5 e_g^2$). Co^{2+} ion is in the HS state.

method. For Co^{2+} ion, the spin and orbital magnetic moments are $\mu_S = 2.61\mu_B$ and $\mu_L = 1.04\mu_B$, respectively, and for Co^{3+} ion, $\mu_S = 1.84\mu_B$ and $\mu_L = 0.40\mu_B$. The orbital moment of Co^{2+} ion is as much as that of CoO [12,13], and the orbital moment of Co^{3+} is comparable to that of NiO [10,14]. The non-negligible orbital moment, which originates from the localized nature of Co 3d electrons, suggests that YBaCo_2O_5 should fall in a class of strongly correlated electron system like CoO and NiO. The calculated total magnetic moments of $\mu_{\text{tot}} = 3.65\mu_B$ and $2.24\mu_B$ for Co^{2+} and Co^{3+} ion, respectively, are only slightly smaller than the experimental values. Evidently, this interpretation will also be valid for $\text{HoBaCo}_2\text{O}_5$. Suard *et al.* [5] have improperly assigned the NPD measured $\mu_{\text{exp}} = 3.7\mu_B$ and $2.7\mu_B$ in $\text{HoBaCo}_2\text{O}_5$ to Co^{3+} and Co^{2+} ion, respectively. However, their assumptions of spin-only moments and the HS states for both Co^{2+} and Co^{3+} ions are discarded by the present results. To test the calculated results, more experimental works like the x-ray scattering measurement are encouraged, in which separate determination of the spin and orbital moments are possible.

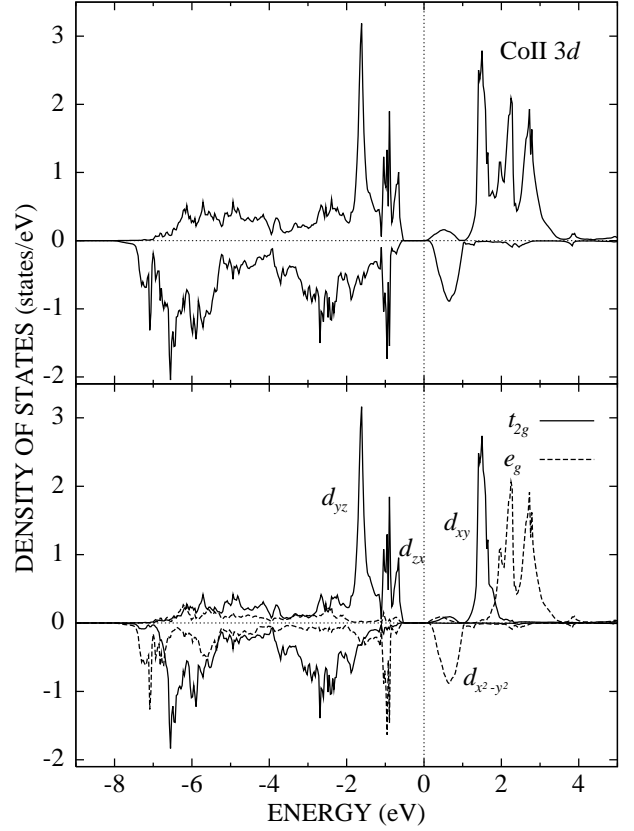


FIG. 3. The LSDA + U PDOS of CoII 3d electrons in the L2 (25 K phase) structure which is antiferromagnetically polarized to that of neighboring CoI. Unoccupied e_g states in the majority-spin bands are clearly visible above E_F . The valency and the 3d electron configuration of CoII site is nominally identified as Co^{3+} and $3d^6$ ($t_{2g}^5 e_g^1$), respectively. Co^{3+} ion is in the IS state.

In Fig. 4, we have plotted the geometry of the orbital ordering which is obtained from the orbital dependent occupancy of the 3d minority-spin states at each Co site. At Co^{2+} sites, the orbitals are aligned along a -axis, while at Co^{3+} sites, the orbitals are along b -axis. This feature is understandable by considering that the bond length of $d(\text{Co}^{2+}\text{-O})$ is larger in a -axis than in b -axis and *vice versa* for that of $d(\text{Co}^{3+}\text{-O})$. As for the charge ordering configuration, Co^{2+} and Co^{3+} chains of a stripe type are formed in the ab plane along b -axis, which are alternating in the a and c direction [1,5]. This is in contrast to the charge ordering observed in the isostructural YBaMn_2O_5 . In YBaMn_2O_5 , the $\text{Mn}^{2+}/\text{Mn}^{3+}$ orders in a checkerboard type [15]. This difference gives rise to the different magnetic structures: G -type AFM phase for YBaCo_2O_5 and G -type ferrimagnetic phase for YBaMn_2O_5 . The theoretical result of the charge and orbital ordering geometry coincides with the experimentally proposed one [1,5]. Thus, it can be inferred that the deformed bond lengths of $d(\text{Co-O})$ determine the charge and orbital ordering geometry.

The G -type AFM ordering in YBaCo_2O_5 is consistent

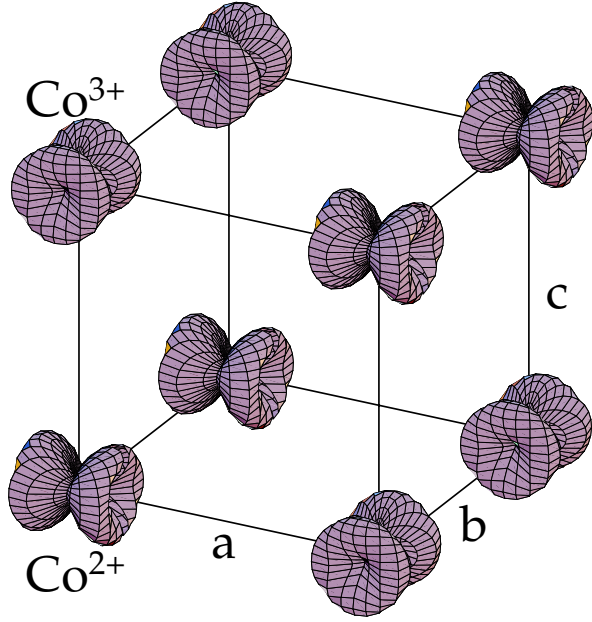


FIG. 4. The orbital ordering geometry of the occupied minority-spin states at each Co site. At Co^{2+} sites, $3d$ orbitals are aligned along the a -axis while at Co^{3+} sites, along the b -axis.

with the above charge and orbital ordering geometry. In the Co^{3+} chains, the kinetic-exchange energy gain between the occupied d_{yz} and d_{zx} states and the empty $d_{x^2-y^2}$ state for the AFM configuration of neighboring sites stabilizes the AFM spin ordering. In a similar way, the AFM ordering between neighboring Co^{3+} and Co^{2+} ions can be explained. The AFM ordering in the Co^{2+} chains, however, is hard to understand in terms of the direct kinetic-exchange gain, because the overlap integral between two neighboring Co^{2+} ions would be negligible as seen in Fig. 4. Instead, the AFM interaction in the Co^{2+} chains is expected to be derived indirectly via the Co^{2+} - Co^{3+} and Co^{3+} - Co^{3+} AFM interactions.

As mentioned above, the structural transition plays a crucial role in determining the ground state properties of YBaCo_2O_5 . Although the tetragonal to orthorhombic structural transition occurs simultaneously with the G -type AFM transition at $T_N \sim 330$ K, the structural deformation is not significant above 220 K. Only near $T_{\text{CO}} \sim 220$ K, the lattice splitting between a - and b -axis becomes pronounced and the charge and orbital ordering emerges with the Co^{2+} spin state transition from the low to high spin. Furthermore, it is known that the long-range charge ordering and the spin state transition are very sensitive to the oxygen stoichiometry [1]. Therefore, the structural distortion is thought to be responsible for the orderings and the spin state transition by inducing different local environment at each Co ion site. This feature implies that the electron-lattice interaction is very important in this system. A detailed study on

the electron-phonon interaction effects in YBaCo_2O_5 is urgently demanded.

In conclusion, we have performed the LSDA + U calculations for a new spin-charge-orbital-lattice coupled system YBaCo_2O_5 . It is found that the $\text{Co}^{2+}/\text{Co}^{3+}$ charge and orbital ordering and the Co^{2+} HS state transition are closely correlated with the lattice distortion from the tetragonal to orthorhombic structure. The orbital moment has a substantially large contribution to the total magnetic moment. All of the effects of the Coulomb correlation, the spin-orbit coupling, and the electron-phonon interaction should be properly taken into account to understand physical properties of YBaCo_2O_5 .

Acknowledgements— This work was supported by the KOSEF (1999-2-114-002-5) and by the Brain Korea 21 Project.

-
- [1] T. Vogt, P. M. Woodward, P. Karen, B. A. Hunter, P. Henning, and A. R. Moodenbaugh, Phys. Rev. Lett. **84**, 2969 (2000).
 - [2] W. Zhou, C. T. Lin, and W. Y. Liang, Adv. Mater. **5**, 735 (1993); W. Zhou, Chem. Mater. **6**, 441 (1994).
 - [3] C. Martin, A. Maignan, D. Pelloquin, N. Nguyen, and B. Raveau, Appl. Phys. Lett. **71**, 1421 (1997).
 - [4] A. Maignan, C. Martin, D. Pelloquin, N. Nguyen, and B. Raveau, J. Solid State Chem. **142**, 247 (1999).
 - [5] E. Suard, F. Fauth, V. Caignaert, I. Mirebeau, and G. Baldinozzi, Phys. Rev. B **61**, R11 871 (2000).
 - [6] M. A. Korotin, S. Yu. Ezhov, I. V. Solovyev, V. I. Anisimov, D. I. Khomskii and G. A. Sawatzky, Phys. Rev. **54**, 5309 (1996); and references therein.
 - [7] D. Akahoshi and Y. Ueda, J. Phys. Soc. Jpn. **68**, 736 (1999).
 - [8] S. K. Kwon and B. I. Min, Phys. Rev. Lett. **84**, 3970 (2000).
 - [9] A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, Phys. Rev. B **52**, R5467 (1995). For review, see V. I. Anisimov, F. Aryasetiawan, and A. I. Liechtenstein, J. Phys.: Condens. Matter **9**, 767 (1997).
 - [10] S. K. Kwon and B. I. Min, "Unquenched large orbital magnetic moment in NiO ", Phys. Rev. B (in press).
 - [11] The valency assignments are nominal, because the number of occupied d -electrons inside the atomic sphere of Co is not an integer due to the hybridization with other bands (see Table I).
 - [12] A. Svane and O. Gunnarsson, Phys. Rev. Lett. **65**, 1148 (1990).
 - [13] I. V. Solovyev, A. I. Liechtenstein, and K. Terakura, Phys. Rev. Lett. **80**, 5758 (1998).
 - [14] V. Fernandez, C. Vettier, F. de Bergevin, C. Giles, and W. Neubeck, Phys. Rev. B **57**, 7870 (1998).
 - [15] F. Millange, E. Suard, V. Caignaert, and B. Raveau, Mater. Res. Bull. **34**, 1 (1999).